254. *The Photochemistry of Phosphorus Compounds. Part II.*[1] *Far-ultraviolet Absorption Spectra of Some Phosphorus Oxyanions in Aqueous Solution.*

By M. HALMANN and I. PLATZNER.

The absorption spectra of solutions of potassium dihydrogen phosphate, potassium and sodium hydrogen phosphates, tetrasodium pyrophosphate, sodium tripolyphosphate, and sodium trimetaphosphate in solvents containing water or deuterium oxide, in the range 320—180 mμ, are composed of both weak bands (above 200 mμ), probably due to internal electronic transitions, and steep absorption edges (below 200 mμ), tentatively assigned to a " charge transfer to solvent " (CTTS) type of transition. The absorption maxima of the steep edges are below 180 mμ. The edges are strongly shifted to shorter wavelength by decrease in temperature, or by substitution of deuterium oxide or aqueous methanol for water as solvent, while such changes have no similar effect on the weak absorption bands above 200 mμ. The spectra of potassium dihydrogen phosphate and of sodium trimetaphosphate (cyclic trimer) are comprised of at least three bands.

THE electronic transitions involved in the absorption of ultraviolet light by phosphoric acid and its anions have not been elucidated. Ali reported that various phosphates in aqueous solution had a very weak absorption maximum at 250 to 300 mμ,[2] while steeply ascending absorptivity for such solutions was found to start below 220 mμ.[3] In the present work, the absorption spectra of various simple phosphorus oxyanions have been measured, the effect of change in temperature and solvent composition having been particularly studied.

The absorption spectra of the dihydrogen phosphate, hydrogen phosphate, pyrophosphate, trimetaphosphate, and tripolyphosphate ions, all in aqueous solution at 25°, in the 320—180 mμ range, are presented in Fig. 1. All the anions show a sharp absorption edge below *ca.* 190 mμ. The dihydrogen phosphate and the trimetaphosphate ions have shallow, weak, absorption maxima in the 280 and 200 mμ regions.

RESULTS

Phosphoric Acid.—Solutions of phosphoric acid do not obey the Beer–Lambert Law; dilution with water causes increased absorptivity (see Table 1). The same effect had been found for sulphuric acid,[4] and is attributed to the acid–base equilibrium in aqueous solution which causes formation of the monoanion, the absorptivity of which is much higher than that of the neutral acid. Thus, most of the observed absorptivity of phosphoric acid in aqueous solution must be due to the dihydrogen phosphate ion.

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[1] Halmann, *J.*, 1963, 2853, is to be considered as Part I.

[2] Ali, *Indian J. Phys.*, 1939, **13**, 309.

[3] Buck, Singhadeja, and Rogers, *Analyt. Chem.*, 1954, **26**, 1240.

[4] Weeks, Meaburn, and Gordon, *Radiation Res.*, 1963, **19**, 559.

TABLE 1.

Absorptivity (l. mole^{-1} cm.$^{-1}$) of phosphoric acid in water at 25°, for 2·4M- and 0·24M-solutions.

λ (mμ)......	205	200	196	194	192	190	189	188	187	186	185	184	183
2·4M-soln.	0·055	0·06	0·08	0·11	0·18	0·34	0·47	0·64	0·90	1·30	1·75	2·25	2·6
0·24M-soln.					0·49	1·09	1·52	2·15	2·65	3·5	5·1	6·7	8·1

The Dihydrogen Phosphate Ion.—Aqueous solutions of the potassium salt obey the Beer–Lambert Law rigorously, both in respect of changes in concentration and path-length, within the range 320—183 mμ. The absorptivity at the shallow plateau of the spectrum ($\lambda_{\text{max.}} = 270$ mμ; $\varepsilon_{\text{max.}} = 0·25$ l. mole^{-1} cm.$^{-1}$) is similar to that obtained by Ali.[2] The data below 220 mμ have not been reported previously. Between 230 and 200 mμ, a shoulder is clearly noticeable (see Fig. 1).

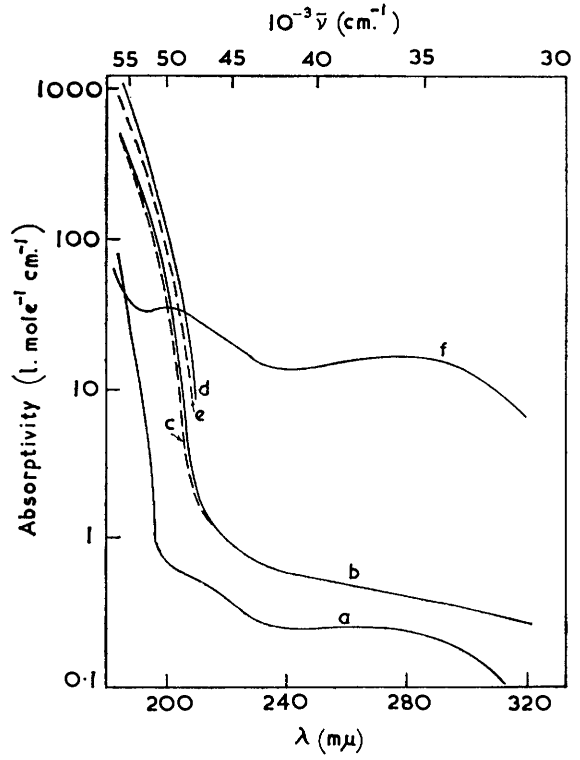

FIG. 1. Far-ultraviolet spectra of aqueous solutions, at 25°, of (a) potassium dihydrogen phosphate, (b) sodium hydrogen phosphate, (c) potassium hydrogen phosphate, (d) sodium pyrophosphate, (e) sodium tripolyphosphate, and (f) sodium trimetaphosphate.

Temperature effects. The spectrum at various temperatures from 1 to 76° is shown in Fig. 2. Changes in temperature have no effect on the shallow plateau at 240—270 mμ, but strongly affect the sharp absorption edge below 220 mμ. Increasing the temperature causes a shift of this edge to longer wavelength. The shoulder at 210 mμ is clearly evident at 1°. The effect of temperature on the wavenumber of absorption ($\bar{\nu}$, in cm.$^{-1}$), at constant absorptivity, is given by the temperature coefficient, $-d\bar{\nu}/dt$. Results for several absorptivities of the dihydrogen phosphate ion are given in Table 2; $-d\bar{\nu}/dT$ decreases with increasing wavenumber.

Solvent effects. Because of the limited solubility of the potassium and sodium salts in organic solvents, and the moderate absorptivity of the dihydrogen phosphate ion above 180 mμ, it was not possible to obtain sufficiently strong solutions of these salts in methanol, ethanol, or acetonitrile for the measurement of their absorption spectra. Attempts to prepare the tetramethyl- or tetraethyl-ammonium salts resulted in samples of insufficient purity. The only effect of solvent on the absorption of the dihydrogen phosphate ion which could be studied was that of substituting deuterium oxide for water; thus, in the 180—190 mμ region (see Fig. 3)

TABLE 2.

Temperature coefficients ($-d\bar{\nu}/dT$) for the absorption edge of aqueous solutions of potassium dihydrogen phosphate, sodium hydrogen phosphate, and sodium trimetaphosphate.

	KH_2PO_4				Na_2HPO_4					$Na_3P_3O_9$
$\bar{\nu}_1$ *	49,580	50,420	53,370	54,560	48,140	48,670	51,600	53,090	54,190	54,200
$\bar{\nu}_2$ †					46,670	47,300	50,300	51,880	53,000	
ε	0·7	1·0	30	80	5·0	10	150	300	450	50
($-d\bar{\nu}/dT$)	27	26	20	19·6	26·5	25·7	23·6	22·8	21·8	22

$\bar{\nu}_1$, $\bar{\nu}_2$ in cm.$^{-1}$; ε in l. mole^{-1} cm.$^{-1}$. * $\bar{\nu}_1$ at 25°. † $\bar{\nu}_2$ at 78°.

the absorption edge is markedly shifted towards shorter wavelengths on substitution with deuterium oxide; at an absorptivity of 25 l. mole^{-1} cm.$^{-1}$, the shift is 660 cm.$^{-1}$ (1·89 kcal. mole^{-1}). At longer wavelengths, the blue-shift disappears; at 220 mμ, the absorptivities in water and in deuterium oxide are equal. At still longer wavelengths, the spectrum in deuterium oxide is red-shifted with respect to water.

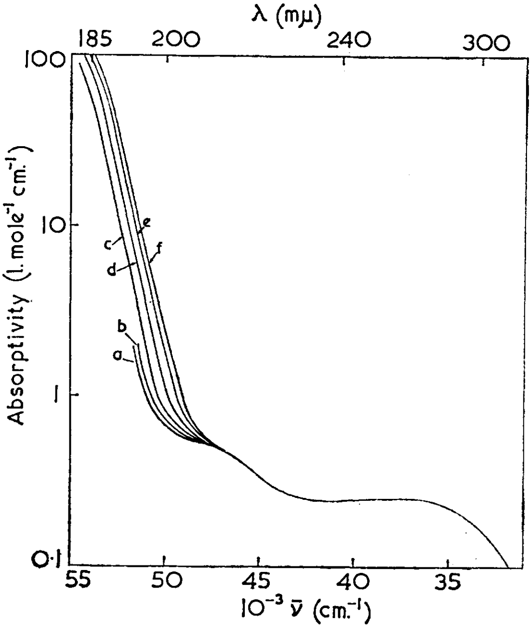

FIG. 2. Far-ultraviolet spectrum of potassium dihydrogen phosphate in water at (a) 1°, (b) 8°, (c) 25°, (d) 45°, (e) 64°, and (f) 76°.

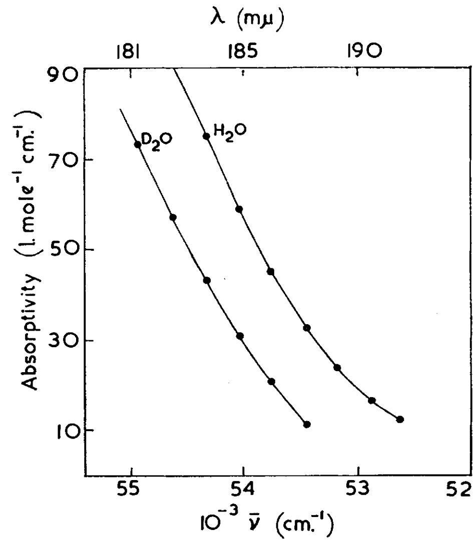

FIG. 3. Far-ultraviolet spectrum of potassium dihydrogen phosphate in water and in deuterium oxide at 24·0° ± 0·5°.

The Hydrogen Phosphate Ion.—The absorptivity of the sodium salt in aqueous solution, over the whole spectral range studied (above 185 mμ), was about 10% higher than that of the potassium salt (see Fig. 1). Both solutions obeyed the Beer–Lambert Law for wide variations in concentration and path-length.

Temperature effects. With increasing temperature, the absorption edge is shifted towards longer wavelengths (Fig. 4), as with the dihydrogen phosphate ion. Again, as with this mono-anion, the shallow absorption above 240 mμ is not affected by changes in temperature. Data for the temperature coefficients of the absorption edge are given in Table 2.

Solvent effects. The absorption edge of the sodium salt below 200 mμ is strongly shifted to shorter wavelengths on substitution of deuterium oxide for water (Fig. 5). At an absorptivity of 200 l. mole^{-1} cm.$^{-1}$, the shift is 760 cm.$^{-1}$ (2·2 kcal. mole^{-1}), which is similar to that observed for the dihydrogen phosphate ion.

In 7·5M-potassium fluoride solution, the spectrum of the sodium salt was almost identical with that in deuterium oxide; the results for the former solvent have, therefore, not been included in Fig. 5. Owing to the relatively high absorptivity of the hydrogen phosphate ion, we were able to obtain also the spectrum of the sodium salt in a 10M-solution of methanol in deuterium oxide. This solvent was chosen because it has been reported that aqueous methanol has an absorption minimum at 184·9 mμ at a concentration of 10M.[4] The result (see Fig. 5) is a marked shift to shorter wavelength even with respect to deuterium oxide or potassium fluoride–water solvent. In aqueous acetonitrile (76% MeCN), the absorption edge is red-shifted with respect to water.

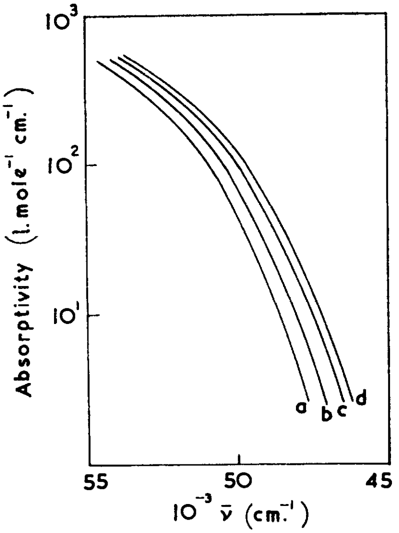

FIG. 4. Far-ultraviolet spectrum of sodium hydrogen phosphate in water at (a) 24°, (b) 45°, (c) 65°, and (d) 78°.

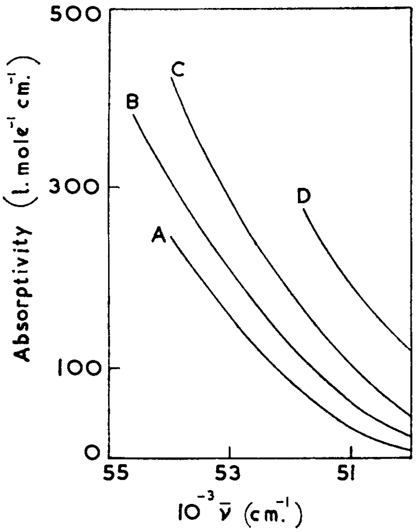

FIG 5. Effect of solvent on the far-ultraviolet spectrum of sodium hydrogen phosphate at 24·0° ± 0·5°. Solvents: (A) 10M-solution of methanol in deuterium oxide; (B) deuterium oxide; (C) water; and (D) acetonitrile (76%) in water.

The Phosphate Ion.—Owing to the acid–base reaction

$$PO_4^{3-} + H_2O = HPO_4^{2-} + OH^-$$

the equilibrium constant of which is the reciprocal of the third dissociation constant, K_3, of phosphoric acid ($K_3 = 4{\cdot}8 \times 10^{-13}$ at 25°),[5] dilute aqueous solutions of the phosphate ion are in fact essentially mixtures of the hydrogen phosphate ion and the hydroxyl ion. The far-ultraviolet absorption of solutions of sodium phosphate [Fig. 6(a)] is therefore due almost completely to the hydroxyl ion. We include, in Fig. 6, our observed spectrum for an aqueous solution of sodium hydroxide, which is in agreement with that previously reported.[4–6]

The Pyrophosphate Ion.—As shown in Fig. 1, the spectrum of the sodium salt in aqueous solution is similar in shape to that of sodium hydrogen phosphate, but is shifted towards longer wavelengths. At constant wavelength, the absorptivity of the pyrophosphate ion is only slightly greater than twice that of the hydrogen phosphate ion, *e.g.*, we have, at 195 and at 200 mμ:

		$HO{\cdot}P(O)O_2^{2-}$	$^{2-}O_2P(O){\cdot}O{\cdot}P(O){\cdot}O_2^{2-}$
Absorptivity (l. mole^{-1} cm.$^{-1}$)	195 mμ	107 ± 7	260 ± 20
	200 mμ	50 ± 5	110 ± 10

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[5] Van Wazer, "Phosphorus and its Compounds," Interscience, New York, 1958, Vol. I, p. 481.
[6] Ley and Arends, *Z. phys. Chem.*, 1929, *B*6, 240; 1932, *B*17, 177.

The absorptivities per phosphorus *atom* for the hydrogen phosphate ion and the pyrophosphate ion are thus approximately equal. In the pyrophosphate ion, electronic effects in one phosphate residue seem to have little influence on electronic excitation in the other phosphate residue. The spectrum of the sodium salt in deuterium oxide shows a marked shift to shorter wavelength compared with that in water (see Fig. 7). At an absorptivity of 60 l. mole^{-1} cm.$^{-1}$, the shift is 630 cm.$^{-1}$ (1·80 kcal. mole^{-1}), which is similar to that for the mono- and di-hydrogen phosphate ions.

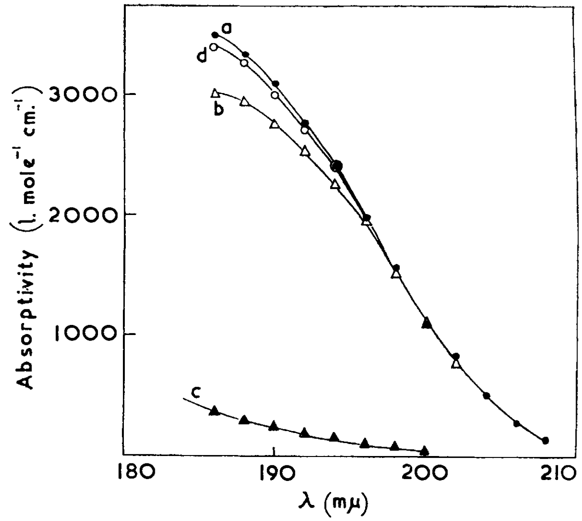

FIG. 6. Far-ultraviolet spectrum at 25° of aqueous solutions of (a) sodium phosphate, (b) sodium hydroxide, and (c) sodium hydrogen phosphate. The data for sodium hydroxide below 192 mμ are taken from ref. 4. The sum of the absorptivities from curves (b) and (c) is given in (d).

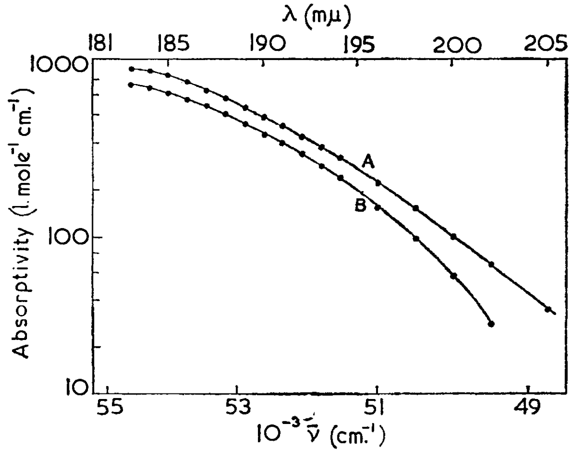

FIG. 7. Far-ultraviolet spectrum of sodium pyrophosphate, at 24 ± 1°, in (A) water and (B) deuterium oxide.

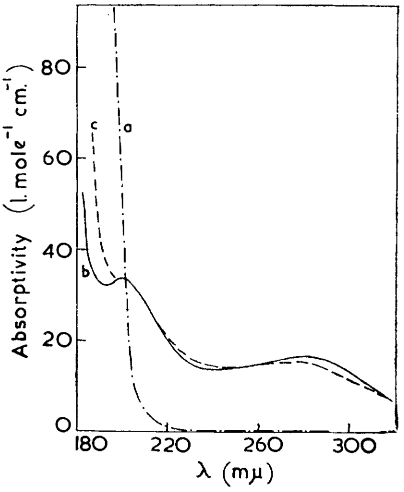

FIG. 8. Far-ultraviolet spectra, in water, of (a) 5·8 × 10^{-3}M-sodium tripolyphosphate at 25°, and sodium trimetaphosphate (b) at 2·5°, and (c) at 71°.

Sodium Tripolyphosphate, $Na_5P_3O_{10}$.—Aqueous solutions of the linear trimer of phosphoric acid, $Na_5PO_3O_{10},6H_2O$, did not obey the Beer–Lambert Law; dilution caused an increase in absorptivity (see Table 3). The general shape of the spectrum [Fig. 8(a)] is similar to that of the hydrogen phosphate ion [Fig. 1(b) and (c)].

Sodium Trimetaphosphate, $Na_3P_3O_9$.—The spectrum of aqueous solutions of the cyclic trimer

TABLE 3.

Absorptivity (l. mole^{-1} cm.$^{-1}$) of sodium tripolyphosphate in water at 25°, at two concentrations.

λ (mμ)	200	198	196	194	192
$4{\cdot}4 \times 10^{-2}$M-soln.	40	66	100	150	215
$5{\cdot}8 \times 10^{-3}$M-soln.	66	100	140	195	270

of phosphoric acid, $Na_3P_3O_9$, obeyed the Beer–Lambert Law. The spectrum at 2·5° and at 71° is shown in Fig. 8(b) and (c). Results for the temperature coefficient of the absorption edge at 184·4 mμ are given in Table 2. This steep edge below 190 mμ is markedly shifted to shorter wavelength by decrease in temperature, and thus reveals a pronounced maximum at 200 mμ. There is another shallow maximum at 280 mμ. The spectrum of the trimetaphosphate ion is thus similar to that of the dihydrogen phosphate ion, both spectra clearly showing two electronic transitions before the sharp absorption edge. As seen in Fig. 1, the general shapes of the spectra of the two ions are similar, although the absorptivity of the trimetaphosphate ion above 190 mμ is much more intense.

DISCUSSION

Introduction.—The feature common to all the spectra of the phosphorus oxyanions studied, and which also occurs with other similar oxyanions such as sulphate and perchlorate,[4] is the steep absorption edge starting below 200 mμ. In all the cases studied, the band maximum was below 180 mμ, but in some cases, *e.g.*, in solutions of the hydrogen phosphate ion at higher temperatures, the form of the curve indicated that the maximum was not much below 180 mμ.

The electronic transitions involved in the absorption of light by anions in solution are due either to some internal charge-transfer, as in $\pi^* \longleftarrow n$ or $\pi^* \longleftarrow \pi$ transitions, or to a " charge transfer to solvent " (CTTS) transition.[7-12]

Bands above 200 mμ.—For tetrahedral oxyanions such as arsenate, the lowest-frequency electronic absorption band has been interpreted as an *allowed* transition of the $\pi^* \longleftarrow n$ type,[10a] and should thus be moderately strong. For the dihydrogen phosphate ion, the results do not support this prediction. The first band of potassium dihydrogen phosphate (Fig. 2), having $\lambda_{\text{max.}} = 270$ mμ and $\varepsilon_{\text{max.}} = 0{\cdot}25$ l. mole^{-1} cm.$^{-1}$, could be due to an $\pi^* \longleftarrow n$ transition, but it is obviously not a strong band. A second weak band at *ca.* 200 mμ is clearly observed as a shoulder of the steep absorption edge, and becomes pronounced at low temperature (see Fig. 2). In crystalline potassium dihydrogen phosphate, an absorption maximum was reported at 220 mμ; this band in the dideuterium compound was shifted to longer wavelength.[13] The same effect has been observed in the present work for the first (longest wavelength) band of the dihydrogen phosphate in solution; the band at 270 mμ was red-shifted on passing from water to deuterium oxide as solvent. The decrease in the energy required for electronic excitation of the heavier ion $D_2PO_4^-$, compared with $H_2PO_4^-$, is to be expected, because of the larger mass-effect on the vibrational terms of the excited electronic state. In diatomic molecules, isotopic substitution by heavier atoms always causes a red-shift of the absorption bands.[14]

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[7] Jortner, Raz, and Stein, *J. Chem. Phys.*, 1961, **34**, 1455.

[8] Platzmann and Franck, in " Farkas Memorial Volume," Weizmann Science Press, Jerusalem, 1952, p. 21.

[9] Griffiths and Symons, *Trans. Faraday Soc.*, 1960, **56**, 1125; Burak and Treinin, *ibid.*, 1963, **59**, 1490; *J. Chem. Phys.*, 1963, **39**, 189.

[10] (*a*) McGlynn and Kasha, *J. Chem. Phys.*, 1956, **24**, 481; (*b*) Strickler and Kasha, *ibid.*, 1961, **34**, 1077; (*c*) Meyerstein and Treinin, *Trans. Faraday Soc.*, 1961, **57**, 2104.

[11] (*a*) Doucet, *Compt. rend.*, 1943, **216**, 198; (*b*) Treinin, Ph.D. Thesis, Hebrew University, Jerusalem, 1958; (*c*) Halmann and Platzner, *Proc. Chem. Soc.*, 1964, 261.

[12] Stein and Treinin, *Trans. Faraday Soc.*, 1959, **55**, 1086, 1091.

[13] Deshotel, *J. Opt. Soc. Amer.*, 1960, **50**, 864; Sliker and Burlage, *J. Appl. Phys.*, 1963, **34**, 1837.

[14] Herzberg, " Molecular Spectra and Molecular Structure. Vol. I. Spectra of Diatomic Molecules," Van Nostrand, Princeton, New Jersey, 1950.

Bands below 200 mμ.—The steep absorption edge of the dihydrogen phosphate ion below 210 mμ is strongly solvent-dependent. The blue-shift in deuterium oxide, aqueous fluoride solutions, or aqueous methanol, and the red-shift in aqueous acetonitrile, are similar to those found for the absorption bands of halide ions, which seem to involve CTTS-type transitions.[8,9,11] Substitution of deuterium oxide for water had no effect on the bands of the nitrate ion,[11c] while substitution of ethanol caused a red-shift in these bands,[10] which were assigned as $\pi^* \leftarrow n$ or $\pi^* \leftarrow \pi$ transitions. We, therefore, conclude that the steep absorption edge of the dihydrogen phosphate ion, and probably also of the other phosphorus oxyanions, is due to a CTTS transition. The negative values of $d\bar{\nu}/dt$ are also in agreement with the theory of CTTS spectra.

The onset of the absorption edge for the hydrogen phosphate ion occurs at a much longer wavelength than for the dihydrogen phosphate ion. The energy required to raise an electron from the ground state of the ion to the electronically excited state is thus lower for the hydrogen phosphate than for the dihydrogen phosphate ion. This must be connected with the lower ionisation potential of the former; the values of the ionisation potentials are as yet unknown, but it is to be expected that the hydrogen phosphate ion, being doubly charged, will have the lower ionisation potential, owing to the greater electrostatic repulsion.

Solvent Effects.—For CTTS-type transitions of polyvalent anions, Treinin[15] has developed a relationship between the frequencies of the absorption band, at a given absorptivity, of a given anion in a given solvent, with the frequency of the band, at the same $\varepsilon/\varepsilon_{\text{max.}}$ value, of iodide in the same solvent; this relationship held for a series of solvents.

The wavenumbers of absorption of sodium hydrogen phosphate at 25° in various solvents at $\varepsilon = 350$ and 200 l. mole^{-1} cm.$^{-1}$ are given in Table 4, together with the CTTS values (absorption maxima of potassium iodide) in the same solvents. In Fig. 9, the line B, best fitting the points for the mixed solvents methanol–aqueous fluoride solution, and aqueous acetonitrile, is seen to deviate from the lines A and C connecting the water and deuterium oxide points (at $\varepsilon = 350$ and 200 l. mole^{-1} cm.$^{-1}$, respectively). The reason that we feel justified, in the subsequent treatment, in using only the points for water and deuterium oxide at the highest measurable absorptivity (line A) is that, in these mixed solvents, the specific solvation interaction of ions with only one component of the solvent can cause deviations which are not possible in a pure solvent. Similar deviations for mixed solvents have been observed in the $h\nu_\varepsilon$ against CTTS plot for other anions.[9] We also feel justified in preferring line A to line C, because, at a shorter wavelength, interference by the low-energy transitions is probably less severe.

TABLE 4.

Wavenumbers of absorption (in cm.$^{-1}$) of sodium hydrogen phosphate at 25° in various solvents at $\varepsilon = 200$ and 350 l. mole^{-1} cm.$^{-1}$, and of the absorption maxima (in cm.$^{-1}$) of potassium iodide in the same solvents.

	$\bar{\nu}$ (HPO_4^{2-})		
Solvent	$\varepsilon = 200$	$\varepsilon = 350$	$\bar{\nu}_{\text{max.}}$ (I^-)
MeCN (76%) in H_2O	51,050		43,250
H_2O	52,200	53,470	44,200
D_2O	52,950	54,300	44,600 *
Aq. 7·5M-KF soln.	53,000		44,650
MeOH (40%) in D_2O	53,600		45,150

* Our result for the absorption maximum of KI in D_2O is equal to that previously determined.[11]

The slope, $\beta = \Delta\bar{\nu}\ (HPO_4^{2-})/\Delta\bar{\nu}\ (I^-) = 840/400 = 2{\cdot}1$, of line A in Fig. 9 can be related

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[15] Treinin, *J. Phys. Chem.*, 1964, **68**, 893. We thank Dr. Treinin for a copy of this Paper in advance of publication.

to the charge, z, of the anion, the crystalline radii, R_I and R_X, of iodide and the anion, and the optical and static dielectric constants, D_O and D_S:

$$\beta = \{zR_I[1 - {}^1/_{(2z)} + {}^1/_{(2zD_O)} - {}^1/_{D_S}]\}/[R_X(\tfrac{1}{2} + \tfrac{1}{2}D_O - 1/D_S)].$$

For the hydrogen phosphate ion in water, $z = 2$, $R_I = 2{\cdot}16$ Å, $D_O = 1{\cdot}77$, $D_S = 80$, thus giving a value for the crystalline radius, R (HPO_4^{2-}), of 2·36 Å. There is no report of the direct determination of radius of this ion. For the phosphate ion, PO_4^{3-}, a thermochemical ionic radius of 2·38 Å has been given.[16] Our result for the hydrogen phosphate ion seems to be in accord with the bond distances reported for potassium dihydrogen phosphate.[17]

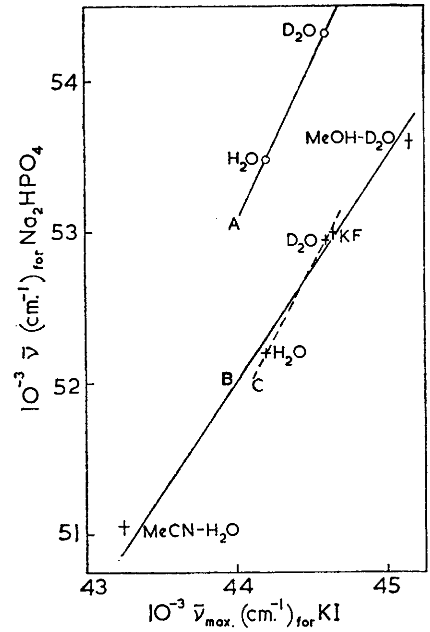

FIG. 9. Wavenumbers (cm.$^{-1}$) of absorption of sodium hydrogen phosphate at 25° in several solvents at (A) $\varepsilon = 350$ and (B) $\varepsilon = 200$ l. mole^{-1} cm.$^{-1}$ plotted against the CTTS values [absorption maxima (cm.$^{-1}$) of potassium iodide] in the same solvents. The line (C) is that fitting only the data for water and deuterium oxide at $\varepsilon = 200$ l. mole^{-1} cm.$^{-1}$.

As shown by Treinin,[16] the slope and intercept of the linear plot in Fig. 9 can be used to derive the vertical ionisation potential, I_X, and the absorption maximum of the anion;

$$h\nu_X = \beta C + I_X - \beta I_I + B(\beta - 1).$$

Choosing a point on the line at which the wavenumber for the hydrogen phosphate ion, $\bar{\nu}_X$, is 53,500 cm.$^{-1}$ ($\equiv$ 153 kcal. mole^{-1}), the corresponding energy for the iodide ion, C, is 126·5 kcal. mole^{-1}. Inserting $\beta = 2{\cdot}1$, $I_I = 70{\cdot}8$ kcal. mole^{-1}, for the ionisation potential of the iodide ion (electron affinity of the atom),[18] and $B = 35$ kcal. mole^{-1}, for the binding energy of the electron to the polarised medium in its excited state,[12] we obtain $I_X = -3$ kcal. mole^{-1} for the vertical ionisation potential of the hydrogen phosphate ion. No data for this quantity appear to have been reported. Our results for R_X and I_X depend critically on the value chosen for the slope. By taking $\beta = 1{\cdot}5$, which gives a better fit with the results for mixed solvents in Fig. 9, we obtain $R_X = 3{\cdot}2$ Å for the ionic radius of the hydrogen phosphate ion, which is rather high, and $I_X \sim +50$ kcal. mole^{-1}. A positive ionisation potential for a doubly charged negative ion seems absurd; in the process $HPO_4^{2-} \longrightarrow HPO_4^- + e^-$, energy must be released.

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[16] Kapustinski, *Quart. Rev.*, 1956, **10**, 286.
[17] Bacon and Pease, *Proc. Roy. Soc.*, 1955, *A*, **230**, 359.
[18] Steiner, Michael, and Branscomb, *J. Chem. Phys.*, 1962, **37**, 1200.

Using the above data for the ionic radius and the ionisation potential of the hydrogen phosphate ion, a prediction of the hitherto unknown absorption maximum for this ion can be made, by using the formula of Treinin for divalent anions in aqueous solution at 25°:[15]

$$
\begin{aligned}
h\nu_{\text{max.}} &= I_{\text{X}} + 465/R_{\text{X}} - 29/R_{\text{X}}^5 - 35 \\
&= -3 + 465/2{\cdot}36 - 29/(2{\cdot}36)^5 - 35 \\
&= 160 \text{ kcal. mole}^{-1} \ (\equiv 56{,}000 \text{ cm.}^{-1} \text{ or } 178 \text{ m}\mu).
\end{aligned}
$$

This value seems reasonable from the appearance of the steep absorption edge of sodium hydrogen phosphate solutions. It should thus be possible to observe this absorption maximum with a vacuum-ultraviolet spectrophotometer, by using very thin layers of solution.

Temperature Effects.—Changes in temperature over the range 0—80° had no appreciable effect on the weak absorption bands of the hydrogen phosphate and dihydrogen phosphate ions, or on the two bands of the trimetaphosphate ion, all above 200 mμ. On the other hand, the steep absorption edge for these ions below 200 mμ was strongly shifted towards longer wavelength by increase in temperature (see Figs. 2, 4, and 8). Values of $-\mathrm{d}\bar{\nu}/\mathrm{d}T$ for aqueous solutions of potassium dihydrogen phosphate, sodium hydrogen phosphate, and sodium trimetaphosphate are presented in Table 2; in the region of the steep absorption edge, $-\mathrm{d}\bar{\nu}/\mathrm{d}T$ decreases with increasing wavenumber. Plots of $-\mathrm{d}\bar{\nu}/\mathrm{d}T$ against wavenumber for the hydrogen phosphate and dihydrogen phosphate ions, for $T = 25°$, are given in Fig. 10. For bands due to CTTS-type transitions, it has been shown that extrapolation of the line for $-\mathrm{d}\bar{\nu}/\mathrm{d}T$ against $\bar{\nu}$, at constant temperature, $-\mathrm{d}\bar{\nu}/\mathrm{d}T = 0$ yields a wavenumber which can be related to the ionic radius and to the vertical ionisation potential of the ion.[7,12]

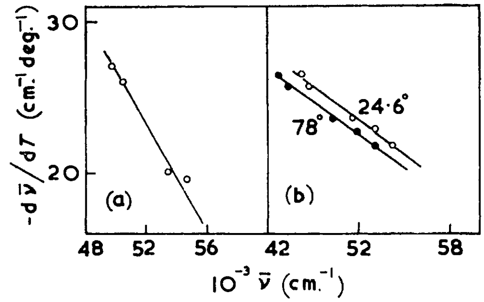

FIG. 10. Temperature coefficients, $\mathrm{d}\bar{\nu}/\mathrm{d}T$, as a function of wavenumber (cm.$^{-1}$) for aqueous solutions of (a) potassium dihydrogen phosphate at 25° and (b) sodium hydrogen phosphate at 24·6° and at 78°.

Assuming a crystalline ionic radius of 2·5 Å for the dihydrogen phosphate ion, and that the steep absorption edge of the ion in water is due to a CTTS transition, then the theory of the effect of temperature on such transitions[12] permits a calculation of the hitherto unknown absorption maximum and ionisation potential of this ion. The unknown energy, $h\nu_{\text{max.}}$, of the absorption maximum, and the energy $h\nu_0$ (8·2 ev) ($\bar{\nu}_0 = 66{,}000$ cm.$^{-1}$), obtained from extrapolation of the linear plot of Fig. 10(a) to $-\mathrm{d}\bar{\nu}/\mathrm{d}T = 0$, are related to the ionisation potential of the ion, the solvation energy, L_{X}, of the radical H_2PO_4, and the ratio, α, of the radius, r, of the ionic cavity to the crystallographic radius, R. The value of α is usually 1·25.[12]

$$h\nu_{\text{max.}} = E_{\text{X}} - L_{\text{X}} + 0{\cdot}77\, e^2/\alpha R - 1{\cdot}58 \text{ ev} \qquad (a)$$

$$h\nu_0 = E_{\text{X}} - L_{\text{X}} + 0{\cdot}77\, e^2/R - 1{\cdot}58 \text{ ev} \qquad (b)$$

Therefore

$$h\nu_{\text{max.}} = h\nu_0 + 0{\cdot}77\, e^2[(1/\alpha) - 1]/R = 7{\cdot}3 \text{ ev } (\equiv 59{,}000 \text{ cm.}^{-1} \text{ or } 170 \text{ m}\mu).$$

From eqn. (*b*), on inserting the values $h\nu_0 = 8{\cdot}2$ ev and $L_X = 0{\cdot}3$ ev (assuming that this value is not appreciably different from that reported for many other anions [12]), we obtain $E_X = 5{\cdot}7$ ev for the ionisation potential of the dihydrogen phosphate ion.

The Photochemistry of Solutions of Sodium Phosphate.—Since the concentration of the phosphate ion in aqueous solution is very small, it seems probable that photochemical effects in such solutions, such as the formation of the hydrated electron after irradiation with ultraviolet light,[19] must be due to absorption of the light by the hydroxyl or hydrogen phosphate ions, and not by the phosphate ion.

Conclusions.—The steep absorption edge below 200 mμ for all the phosphates studied appears to be due to a CTTS-type transition. To the extent that the theory of such transitions, which was developed for halide ions, also applies quantitatively to polyvalent ions, estimates can be made of ionic radii, ionisation potentials, and absorption maxima for anions of phosphoric acid.

EXPERIMENTAL

Absorption Spectra.—These were measured with a modified Zeiss PMQII spectrophotometer, specially sealed for work in the far-ultraviolet region down to 180 mμ, which was completely flushed with dry nitrogen gas (99·8% pure) at a rate of 2 l. min.$^{-1}$. The wavelength calibration was checked by using the 253·7 and 184·96 mμ lines of a low-pressure mercury lamp. Fused-quartz absorption cells of 0·01-, 0·1-, 0·5-, 1·0-, 2·0-, and 5·0-cm. path-lengths were used.

Below 185 mμ, special precautions were necessary, to avoid stray-light effects. The path-length and the solvent absorption in the reference cell were limited, so that the slit-width remained below 0·08 mm.; in this way, the spectra obtained for aqueous solutions of perchloric and sulphuric acids were similar to those reported.[4] When a wider slit was used, the absorptivity for these reference substances appeared to decrease below 185 mμ, probably owing to stray light.

Materials. Phosphoric acid, sodium hydrogen phosphate ($Na_2HPO_4,12H_2O$) (both AnalaR; B.D.H.), methanol (spectroscopic grade; B.D.H.), and acetonitrile (spectroscopic grade; Fluka AG) were used without further purification. Potassium dihydrogen phosphate (AnalaR; B.D.H.) and potassium hydrogen phosphate (Baker Analysed) were dried at 80°.

Sodium trimetaphosphate (Albright and Wilson), crystallised three times from aqueous ethanol and dried (P_2O_5), yielded the anhydrous compound. It was analysed by passing an aqueous solution of it through Dowex 50Wx12 cation-exchanger, and then titrating with sodium hydroxide (Found: Equiv., 103. Calc. for $Na_3P_3O_9$: Equiv., 102). Traces of nitrate were shown to be absent by means of the spot-test with brucine or diphenylamine.[20] Sodium tripolyphosphate (Albright and Wilson), crystallised from aqueous ethanol and dried (P_2O_5), yielded the hexahydrate. Water was redistilled from alkaline permanganate and then from phosphoric acid, atmospheric carbon dioxide being excluded. Deuterium oxide (Norsk Hydro-Elektrisk Kvaelstof Akt.) was used without further purification.

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